

Semi - Annual Status Report

Interactions of Radiation
With Planetary Gases

October 1974

NASA Grant No. NGR. 28-004-021



Prepared by

James A.R. Samson
Physics Department
University of Nebraska
Lincoln, NE 68508

N74-77522

(NASA-CR-140792) INTERACTIONS OF
RADIATION WITH PLANETARY GASES
Semiannual Status Report (Nebraska Univ.)
27 p

Unclas
00/99 53143

During the past six months we have continued our study of the interactions of radiation with gases over a broad front. In particular, we have included some very important theoretical work on the angular distribution of electrons. This work has been applied to atomic oxygen. At present we are trying to verify theory at a single wavelength (584 \AA). These are difficult experiments, however, it is important to verify theory so that it can be used in confidence at wavelengths inaccessible to experiment.

Measurements on the Branching Ratios of many gases continue over a large wavelength range. This includes details of electronic states and of vibrational intensities with electronic states. Some of this work has been published, much has yet to be analyzed. Ionization yields and cross sections are being measured and analyzed. No publications have been prepared yet. It is expected that these will appear in print during 1975.

This research program has been extremely productive to date. Abstracts of all talks and publications are listed below covering the period from the last final report.

PHYSICAL REVIEW LETTERS

VOLUME 31

26 NOVEMBER 1973

NUMBER 22

Resonances in the Angular Distribution of Xenon Photoelectrons*

James A. R. Samson and J. L. Gardner

Behlen Laboratory of Physics, University of Nebraska, Lincoln, Nebraska 68508

(Received 19 September 1973)

Measurements are reported of the resonant structure, caused by autoionization, in the angular distribution of xenon photoelectrons. The measurements were made within the autoionizing structure lying between the $^2P_{3/2}$ and $^2P_{1/2}$ ionization thresholds for the wavelength range 956 to 1015 Å. The results show a periodic variation in the asymmetry parameter β with maximum excursions of about +0.9 to -0.9. The overall variation and magnitude of β is in accord with the recent theoretical predictions of Dill.

We report the first measurements of resonant structure, caused by autoionization, in photoelectron angular distributions. Although a number of experimental determinations of photoelectron angular distributions have been reported,¹⁻¹² no measurements exist of the variation of the angular distribution with energy across autoionization resonances. A recent paper by Dill¹³ considered, theoretically, the influence of autoionization on the angular distribution parameter β .¹⁴ This paper gave the important general prediction that β should fluctuate rapidly within the allowed range of +2 and -1 across any autoionizing resonance, atomic or molecular. In particular, β was calculated for xenon across the first autoionizing resonance between the $^2P_{3/2}$ and $^2P_{1/2}$ ionization thresholds. The current experiment was designed to measure the xenon photoelectron angular distributions as a function of wavelength between the $^2P_{3/2}$ and $^2P_{1/2}$ thresholds to compare with the predictions of Dill. The importance of measuring β across a resonant structure was emphasized by Dill as a new and independent method to probe atomic and molecular dynamics.

The experimental technique employed was to measure the angular modulation of the photoelectron count rate within a 6° cone of acceptance in

the plane normal to the beam of partially plane-polarized radiation emerging from the exit slit of a $\frac{1}{2}$ -m Seya-Namioka monochromator. This method has not been previously used. From an expression for the general angular dependence of the photoelectron signal when using partially plane-polarized light,¹⁵ it is readily shown that

$$\left. \frac{d\sigma}{d\Omega} \right|_{x-z \text{ plane}} = \frac{\sigma}{4\pi} \left(1 - \frac{\beta}{2} + \frac{3\beta}{2(g+1)} [(g-1)\sin^2\theta + 1] \right),$$

where the photon beam is traveling along the +y axis, σ is the integrated cross section, θ is the angle of emission measured in the x-z plane from the z axis, and g is the degree of polarization given by I_x/I_z , the ratio of the radiation intensity components in the x and z directions, respectively.

The apparatus is shown schematically in Fig. 1. Electrons formed within the ionization region were allowed to drift in a field-free region through a series of five baffles to a Spiraltron detector, and the resultant pulses were integrated with a rate meter. Since angular distributions were to be determined for xenon in the wavelength range below the $^2P_{1/2}$ ionization threshold, no energy

PHYSICAL REVIEW LETTERS

VOLUME 32

6 MAY 1974

NUMBER 18

Photoelectron Angular Distributions as a Probe of Anisotropic Electron-Ion Interactions*

Dan Dill

Department of Chemistry, Boston University, Boston, Massachusetts 02215

and

Steven T. Manson

Department of Physics, Georgia State University, Atlanta, Georgia 30303

and

Anthony F. Starace

Behlen Laboratory of Physics, The University of Nebraska, Lincoln, Nebraska 68508

(Received 31 December 1973)

Expressions are given for atomic photoelectron angular distributions in LS coupling in which the role of anisotropic final state electron-ion interactions emerges explicitly. Calculations of photoelectron angular distributions for atomic sulfur are presented in which these anisotropic interactions produce clear deviations from the predictions of the Cooper-Zare model. Such effects are expected to be a general feature of photoelectron angular distributions for most open-shell atoms.

We report here expressions for atomic photoelectron angular distributions in LS coupling which exhibit clearly the influence of anisotropic electron-ion interactions. To illustrate these effects we have calculated the angular distributions of electrons photoionized from atomic sulfur, for which these anisotropic final-state interactions are large. These effects take the form of pronounced differences between the distributions of photoelectron groups corresponding to alternative LS -term levels of the residual ion. This result is to be contrasted with that of the Cooper-Zare (CZ) model,¹ in which the role of final-state interactions is not considered: No dependence on the ionic term level is predicted. The past success of the CZ model in confirming measurements^{2,3} is due to the fortuitous circumstance that the measurements have dealt with

closed-shell atoms, for which we show that angular momentum and parity conservation impose severe restrictions on the effects of any anisotropic interactions.

Our results are aimed on the one hand at theorists engaged in photoionization cross section calculations that include electron correlation. The criteria for assessing the importance of anisotropic interactions are given in terms of interaction parameters provided by such calculations. On the other hand, we wish to emphasize to experimentalists this new dynamical information on final-state interactions that can emerge through the study of open-shell atoms.

Our analysis is based on the resolution of the angular distribution into separate contributions characterized by the alternative values j_i of the angular momentum transferred in the photoioni-

Experimental vibrational intensity distributions for continuum photoionization to the $X^2\Sigma^+$, $A^2\Pi$, and $B^2\Sigma^+$ states of CO^+ and N_2^+

J. L. Gardner and James A. R. Samson

B 210 Laboratory of Physics, University of Nebraska, Lincoln, Nebraska 68508

(Received 31 December 1973)

Vibrational intensity distributions have been deduced from vacuum-ultraviolet photoelectron spectra ever since the vibrational structure has been resolved.^{1,2} Most spectra have been recorded from undispersed radiation sources, allowing the possibility of electrons generated from impurity lines to be present along with the desired spectrum, and with electron energy analyzers whose transmission as a function of energy has been assumed. Pressure sensitive effects, notably modification of the spectrum by resonant scattering through negative ion states,³ and differential scattering out of the electron beam for electrons of different energies,⁴ may also have been unaccounted for.

We have recorded photoelectron spectra from CO and N_2 using dispersed 584 Å and 537 Å radiation from a DC discharge in helium, with a cylindrical mirror analyzer, described elsewhere,⁴ whose transmission as a function of energy has been calibrated. (The calibration procedure is described in Ref. 4. The light source used for the present calibration was a duoplasmatron.⁵ Argon gas was used in the discharge which produced a large number of Ar II lines. Electron counting techniques may be used with this source, and the present calibration is felt to be more accurate than that previously obtained with a condensed spark discharge.⁴) The gas pressure in the analyzer was held at less than 0.1 mTorr. The spectra were recorded at a constant 3 eV pass energy with the aid of a preretarding lens, to reduce scattering effects⁴ and to provide a constant resolution of 45 meV so that peak areas could be used directly as a measure of the photoelectron intensity.

The experimental vibrational intensities, corrected for the transmission of the analyzer, are tabulated in Table I together with theoretical Franck-Condon factors⁶; all data are normalized to 100 at the strongest peak in each vibrational band. Up to 15 spectra have been included in each distribution; the errors represent statistical fluctuations in the count rates only. The results for the $B^2\Sigma^+$ states include only 537 Å spectra, as anomalous distributions, caused by resonant scattering through negative ion states, could be seen in all the 584 Å spectra in the energy range covered by the $B^2\Sigma^+$ transitions. This was true even at the lowest useable pressures in the analyzer. The results for the $X^2\Sigma^+$ and $A^2\Pi$ ionic states include both 584 Å and 537 Å spectra, thus minimizing errors in the determination of the transmission through the analyzer as a function of the electron energy. The error in the transmission calibration could be as high as 15% across the energy range covered by the $A^2\Pi$ electrons at each wavelength. No

significant differences in the distributions at the two wavelengths could be seen for each of the $X^2\Sigma^+$ and $A^2\Pi$ states.

The agreement between the experimental distributions and the Franck-Condon factors is good for the $\text{CO}^+ X^2\Sigma^+$ and $B^2\Sigma^+$ states. The experimental intensity across the $\text{CO}^+ A^2\Pi_i$ state is seen to be consistently higher than the Franck-Condon factor as the vibrational quantum number increases, although part of this trend could be due to errors in the transmission calibration. The discrepancy between the experimental and theoretical intensities at the $\nu=5$ level of the $A^2\Pi_i$ state is probably caused by crossing of the $\text{CO}^+ A$ and X potential curves. Singh and Rai⁷ predicted a perturbation at the $\text{CO}^+ A$, $\nu=5$ level; this has not been previously observed.

The experimental vibrational intensity distributions for the $A^2\Pi_u$ and $B^2\Sigma_u^+$ states of N_2^+ agree reasonably well with the Franck-Condon factors (apart from $\nu=7$ of the $A^2\Pi_u$ state), with a possible consistent deviation about $\nu=4$ of the $A^2\Pi_u$ state. This deviation, together with the trend in the $A^2\Pi_i$ state of CO^+ , may be explicable by the variation of the electronic transition moment with the internuclear separation of the atoms and/or with the energy of the emitted electron, as in the case of hydrogen.⁸

TABLE I. Vibrational intensities and Franck-Condon factors for transitions (N_2 , CO) $X^1\Sigma^+$, $\nu=0$, to the ionic levels indicated.

		N_2		CO	
		Experimental intensity	FCF ⁶	Experimental intensity	FCF
$X^2\Sigma^+$	$\nu=0$	100.0	100.0	100.0	100.0
	1	6.94 ± 0.66	9.27	3.46 ± 0.27	3.84
	2	0.32 ± 0.21	0.59		
$A^2\Pi$	$\nu=0$	87.1 ± 3.1	84.9	39.4 ± 2.4	37.3
	1	100.0 ± 2.8	100.0	83.4 ± 1.4	82.1
	2	76.3 ± 1.5	68.0	100.0 ± 3.1	100.0
	3	43.5 ± 2.9	35.3	86.7 ± 1.6	89.5
	4	19.1 ± 2.4	15.7	67.8 ± 1.9	66.0
	5	7.09 ± 0.77	6.37	50.3 ± 1.7	42.6
	6	2.51 ± 0.40	2.43	24.2 ± 1.3	25.0
	7	1.70 ± 0.34	0.89	14.8 ± 0.5	13.7
	8	0.37 ± 0.17	0.32	8.31 ± 0.47	7.15
	9			5.08 ± 0.97	3.59
	10			2.53 ± 0.56	1.75
	11			1.03 ± 0.22	0.84
$B^2\Sigma^+$	$\nu=0$	100.0	100.0	100.0	100.0
	1	9.84 ± 2.51	13.1	35.0 ± 1.0	35.4
	2	0.76 ± 0.94	0.25	7.75 ± 1.61	7.06

Photoelectron angular distributions, cross sections, and branching ratios for atomic oxygen

Anthony F. Starace*

Behlen Laboratory of Physics, The University of Nebraska, Lincoln, Nebraska 68508

Steven T. Manson†

Department of Physics, Georgia State University, Atlanta, Georgia 30303

David J. Kennedy‡

School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332

(Received 30 January 1974)

Theoretical calculations of the angular distribution of photoelectrons ejected from the $2p$ subshell of atomic oxygen for photoelectron kinetic energies $0 < \epsilon < 30$ Ry are presented using both Hartree-Fock (HF) and Herman-Skillman (HS) wave functions. Owing to the weakness of anisotropic electron-ion interactions, as evidenced by small differences between HF photoelectron phase shifts for alternative outgoing channels, the simple HS calculation of the angular-distribution asymmetry parameter is found to agree to within ≈ 0.1 with the HF calculations. Photoionization cross sections and photoelectron branching ratios have also been computed in both the HF and HS approximation for the $2p$ subshell of atomic oxygen in the wavelength range $910 \leq \lambda \leq 100$ Å. Comparison is made with other theoretical calculations and with the experimental branching-ratio measurements of Samson and Petrosky at $\lambda = 584.3$ Å.

I. INTRODUCTION

Dill, Manson, and Starace¹ have shown that the Cooper-Zare theory² for photoelectron angular distributions, while correct for closed-shell atoms, is not appropriate for open-shell atoms except in those cases where the phase shifts for alternative photoelectron channels are the same. We present here theoretical calculations that confirm atomic oxygen as one of these special cases. We find that the use of Herman-Skillman³ (HS) wave functions and the Cooper-Zare theory provides angular distribution asymmetry parameters that are in substantial agreement with those obtained using Hartree-Fock (HF) wave functions and a more rigorous theory¹ for photoelectron angular distributions. We expect similar results for the other atoms having open $2p$ subshells. Thus, the angular distributions of photoelectrons from $2p$ subshells calculated by Manson⁴ using HS wave functions and the Cooper-Zare theory should prove reliable.

We present also new calculations, using both HS and HF wave functions, of the total and partial photoionization cross sections of atomic oxygen. Because these cross sections are of fundamental importance for upper atmosphere physics, they have been calculated by many authors.⁵⁻¹⁰ Following Henry⁷ we plot also photoelectron branching ratios since these are the quantities measured directly in photoelectron spectroscopy. At $\lambda = 584.3$ Å our branching ratios are in reasonable agreement with both the experimental values of Samson

and Petrosky¹¹ and the more accurate close-coupling calculations of Henry.⁷ The calculated angular distributions, cross sections, and branching ratios presented in this paper thus extend and complement existing theoretical data on the photoionization of atomic oxygen.

II. THEORY

Dill and Fano¹²⁻¹⁴ have expressed the differential cross section for photoionization of an unpolarized target as an incoherent sum over contributions corresponding to alternative values of the angular momentum \vec{j}_t transferred by the incident photon to the target:

$$\frac{d\sigma}{d\Omega} = \sum_{j_t} \frac{\sigma(j_t)}{4\pi} [1 + \beta(j_t)P_2(\cos\theta)]. \quad (1)$$

Detailed expressions for the partial cross sections $\sigma(j_t)$ and asymmetry parameters $\beta(j_t)$ are given in Ref. 14 in terms of scattering amplitudes $S_l(j_t)$, where l is the orbital angular momentum of the outgoing photoelectron. The experimentally measured asymmetry parameter β is then given by the following weighted average¹⁴:

$$\beta = \left(\sum_{j_t} \sigma(j_t) \beta(j_t) \right) / \sum_{j_t} \sigma(j_t). \quad (2)$$

For the particular case of LS coupling the general photoionization process via electric dipole interaction,

$$A(l_0^n L_0 S_0 J_0) + h\nu \rightarrow A^*(l_0^{n-1} L_c S_c J_c) + e^-(l, s, j), \quad (3)$$

Continuum ionization transition probabilities of atomic oxygen

James A. R. Samson and V. E. Petrosky

Behlen Laboratory of Physics, University of Nebraska, Lincoln, Nebraska 68508

(Received 21 January 1973)

The technique of photoelectron spectroscopy has been used to obtain the relative continuum transition probabilities of atomic oxygen at 584 Å for transitions from the 1P ground state into the 1S , 1D , and 3P states of the ion. The ratio of the transition probabilities for the 1D and 3P states relative to the 1S state of the ion are 1.57 ± 0.14 and 0.82 ± 0.07 , respectively. In addition, transitions from the excited $O_2(a^1\Delta_g)$ state into the $O_2^+(^1\Delta_g)$ and $^1\Delta_g$ states were observed. The adiabatic ionization potential of $O_2^+(^1\Delta_g)$ was measured as 18.803 ± 0.006 eV.

INTRODUCTION

Many theoretical investigations of the photoionization of atomic oxygen have been carried out.¹⁻⁵ These include cross-section calculations, transition probabilities for specific ionic states, and calculations of the angular distribution of the ejected photoelectrons. The experimental verification of these calculations is difficult because of the experimental problems in dealing with a transient species such as atomic oxygen. In addition to supporting a particular theoretical model, the experimental results on the photoionization of atomic oxygen are extremely important in upper atmospheric studies since a prime constituent of the Earth's atmosphere at about 200 km is atomic oxygen.

Previous experimental studies on photon interaction with atomic oxygen have been confined to absorption studies. Huffman *et al.*⁶ obtained an absorption spectrum between 600 and 1000 Å while Cairns and Samson¹⁰ and Comes *et al.*¹¹ measured absolute cross sections at discrete emission lines in the same wavelength interval. More recently Jonathan *et al.*^{12,13} have observed the photoelectron spectrum of atomic oxygen at 584 Å and Dehmer *et al.*¹⁴ have studied the ions produced by photoionization in a mass spectrometer.

The present investigation involves the technique of photoelectron spectroscopy. This is an extremely powerful method for measuring the relative transition probabilities for populating the various ionic states available for the given photon energy. However, to obtain meaningful results the collection efficiency of the electron energy analyzer must be calibrated as a function of the electron energy and the analyzer must not discriminate against electrons with differing angular distributions. To date this has not been done. The present work reports absolute transition probabilities for the photoionization transition

$2p^1(^3P) \rightarrow 2p^1(^1D, ^1P)$ relative to transitions to the $2p^3(^1S)$ ground state of the atomic oxygen ion.

EXPERIMENTAL

Atomic oxygen was produced in a microwave discharge (2450 MHz) operating at a power of 40 W and at a pressure of approximately 20 mTorr. Although number densities of the atoms were not measured, similar techniques have produced about 5% dissociation.¹⁰ In addition to atomic oxygen, other species were produced. The parent molecule can be excited into the lowest excited state, the $O_2(a^1\Delta_g)$ state, which lies about 1 eV above the ground $X^3\Sigma_g^-$ state. Molecules in the excited $a^1\Delta_g$ state account for about 5–10% of the products. Other species may be formed such as ozone and O_3 in various vibrational states. However, these were not observed in the present experiment where the discharged gas had to travel about 50 cm through 11-mm i.d. pyrex tubing. Quartz tubing was used in the microwave cavity. The tubing was treated with dilute phosphoric acid to minimize the recombination of atomic oxygen. Thus, three species were formed, namely, $O(^3P)$, $O_2(X^3\Sigma_g^-)$, and $O_2(a^1\Delta_g)$. Figure 1 shows the microwave discharge and the atomic oxygen flow in relation to the photoelectron spectrometer.

The electron energy analyzer was a cylindrical mirror design based on the analysis given by Karras *et al.*¹⁵ Slit-to-slit focusing was adopted with an entrance trajectory of 54.7° with respect to the axis of the cylinders. This particular angle was chosen because the fraction of the electrons traveling in this direction is directly proportional to the total number of photoelectrons produced regardless of their angular distribution.¹⁶ A retarding/accelerating lens (L) was incorporated so that the electrons would have a fixed pass energy and hence a constant energy resolution. With 2 V between the inner and outer cylinders the full width at half-maximum for argon was 30 meV.

PARTIALLY AUTOIONIZING STATES OF ATOMIC OXYGEN*

JAMES A. R. SAMSON and V. F. PETROSKY

Behlen Laboratory of Physics, University of Nebraska, Lincoln, Neb., 68508, U.S.A.

(First received 21 January 1974; in final form 11 February 1974)

ABSTRACT

The Rydberg states $3d' \ ^3P_{2,1,0}^o$ and $3s'' \ ^3P_{2,1,0}^o$ and the inter-shell transition $2s2p^5 \ ^3P_{2,1,0}^o$, which are forbidden to autoionize on the basis of LS coupling, have been observed in emission spectroscopy and in autoionization spectra produced in the photoelectron spectrum of atomic oxygen.

Jonathan et al.¹ have observed unidentified structure in their 584 Å He I photoelectron spectrum of atomic oxygen. They concluded that the structure was caused by impurity lines in undispersed helium light source. However, the strength of the photoelectron structure was surprisingly high. In the present work, it is shown that the structure is indeed caused by impurity lines from the light source; in particular, from O I resonance lines caused by an O₂ impurity. These resonance lines populate Rydberg states lying above the first ionization potential of atomic oxygen. The states responsible for the structure are the Rydberg levels $3d' \ ^3P_{2,1,0}^o$ and $3s'' \ ^3P_{2,1,0}^o$ and the inter-shell transition $2s2p^5 \ ^3P_{2,1,0}^o$. The states subsequently de-excite via the two competing paths of emission and autoionization. When autoionization takes place, an electron is ejected with an energy equal to the difference between the energy of the state and the ionization potential of the continuum interacting with the state (in this case, the ⁴S continuum). The interesting point is that these states are forbidden to autoionize on the basis of LS coupling. However, in the present work, the states are observed both in emission spectroscopy and in photoelectron spectroscopy.

Recently, these autoionizing forbidden states have been observed by Dehmer et al.² in their photoionization-mass-spectrometric studies. By the use of the Hopfield continuum, they studied the photoionization of atomic oxygen as a function of wavelength over the range 912 to 660 Å. They observed autoionizing structure at all the allowed transitions, including the LS forbidden states discussed here.

* Presented at the Meeting of the Division of Electron and Atomic Physics, Yale University, 10-12 December 1973.

PHOTOELECTRON SPECTROSCOPY OF N_2 AND CO WITH DISPERSED NeI RADIATION*

J.L. GARDNER and James A.R. SAMSON
*Becken Laboratory of Physics, University of Nebraska
Lincoln, Nebraska 68508, U.S.A.*

Received 4 March 1974

High resolution photoelectron spectra have been recorded from N_2 and CO with a fully calibrated energy analyzer at both the 736 and 744 Å NeI lines. Observation of electrons from transitions to the $v = 11$ level of the $CO^+ X^2\Sigma^+$ ground state is reported for the first time. Relative intensities of all vibrational peaks appearing in each spectrum are given.

It has been known for some time that the photoelectron spectra of N_2 and CO recorded with NeI radiation (736 and 744 Å) show vibrational structure extended considerably beyond that produced by continuum ionization [1]. This structure is caused by transitions through an intermediate neutral electronic state which subsequently autoionizes. Previously reported spectra were taken with comparatively poor resolution and with undispersed radiation so that two overlapping spectra 177 meV apart are produced.

We have recorded spectra from CO and N_2 at each of the NeI lines after dispersion by a 1/2 m Seya-Namioka monochromator. The energy analyzer, which has been described in the literature [2], is of cylindrical mirror type with a pre-retarding lens; the spectra were recorded at a pass energy of 0.75 eV, yielding a resolution of the order of 10 meV. The scanning voltage was produced by a digitally programmed stepping motor-potentiometer combination which was synchronized to the advance of a multichannel store. Energy increments were accurately known from a calibration of the potentiometer voltage versus number of steps.

The transmission of the analyzer was calibrated, as previously described [2], by measuring the count

* Research supported by the National Aeronautics and Space Administration under Grant NGR 28-004-021.

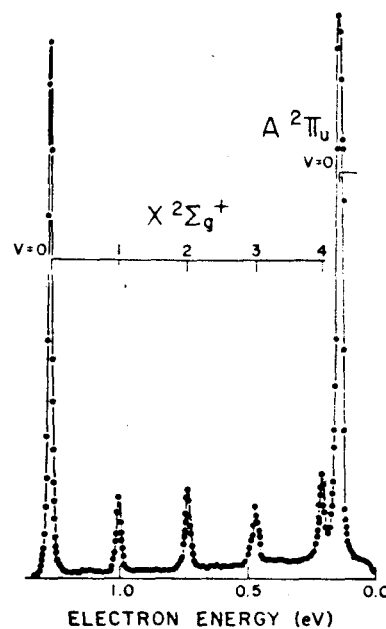


Fig. 1. Photoelectron spectrum recorded from N_2 at 736 Å.

rates of photoelectrons from Ar and Xe at a number of ArII lines produced in a duoplasmatron light source.

The photoelectron spectrum recorded from N_2 at 736 Å is shown in fig. 1. The resolution is sufficient to separate the $N_2^+ X^2\Sigma_g^+$ ($v = 4$) peak from the $A^2\Pi_u$ ($v = 0$) peak, but is not sufficient to resolve the

COLLECTING EFFICIENCY OF A CYLINDRICAL MIRROR ELECTRON ENERGY ANALYZER WITH PRE-RETARDING LENS

J. L. Gardner and James A. R. Samson

Behlen Laboratory of Physics

University of Nebraska

Lincoln, Nebraska 68508 U.S.A.

ABSTRACT

The electron collecting efficiency of a cylindrical mirror energy analyzer incorporating retardation of the electrons prior to analysis has been determined over the range 0 to 30 eV by two methods. The first method requires the use of a vacuum ultraviolet monochromator to produce monoenergetic electrons of different energies; the second method involves measuring the energy-brightness relationship of the retarding optics and should be applicable to any deflection analyzer with pre-retarding optics. The results of the two methods are compared and the limitations of the latter method are discussed.

21.4

Vibrational Intensity Distributions for Continuum
Photoionization of Oxygen

J. L. Gardner and James A. R. Samson
Behlen Laboratory of Physics
University of Nebraska
Lincoln, Nebraska 68508 U.S.A.

We have recently reported experimental vibrational intensity distributions for continuum photoionization of N_2 and CO, mainly at a wavelength of 584 \AA .¹ the purpose of this note is to report similar results for oxygen using both the 584 \AA and 304 \AA helium lines.

The photoionization cross section of oxygen shows a substantial dip in magnitude over a 20 \AA band centered about 590 \AA ;² thus the possibility exists that the 584 \AA photoelectron spectrum of oxygen includes an autoionized contribution and, consequently, the vibrational intensity distributions may not correspond to those of continuum ionization. The oxygen photoionization cross section shows no structure around 304 \AA and purely continuum ionization is expected.

The experimental technique is that reported previously.¹ Photoelectron spectra were recorded at a resolution of 45 meV with dispersed He radiation, using a cylindrical mirror energy analyzer with known transmission properties.

PHOTOION AND PHOTOELECTRON SPECTROSCOPY OF CO AND N₂

J. L. Gardner and James A. R. Samson

Behlen Laboratory of Physics

University of Nebraska

Lincoln, Nebraska 68508 U.S.A.

Abstract:

Dissociative photoionization processes in CO and N₂ have been studied via photoion and photoelectron spectroscopy. Kinetic energy spectra of both the ions and electrons formed in CO and N₂ have been recorded with a calibrated energy analyzer at incident wavelengths of 584, 462, and 304 Å. The 304 Å spectra are correlated in energy and intensity to deduce dissociation products. For CO, the $^2\Sigma^+$ state of CO⁺ formed by removing a σ^2s electron dissociates to the products C⁺ ($2p^2\ ^2P^0$) and O ($3s^1\ ^3D^0$). The N₂ ion and electron spectra at 304 Å both contain evidence for dissociative transitions involving the D $^2\Pi_g$ state of N₂⁺. Energetic N⁺ ions produced upon removal of a g^2s electron are best explained by a dissociation limit of N⁺ ($2p^3\ ^3P^0$) and N($2p^3\ ^4S^0$).

Submitted to: Phys. Rev. A

EFFECTS OF ANISOTROPIC ELECTRON-ION INTERACTIONS
IN ATOMIC PHOTOELECTRON ANGULAR DISTRIBUTIONS

Dan Dill

Department of Chemistry

Boston University

Boston, Massachusetts 02215

and

Anthony F. Starace^{*}

Behlen Laboratory of Physics

The University of Nebraska

Lincoln, Nebraska 68508

and

Steven T. Manson[†]

Department of Physics

Georgia State University

Atlanta, Georgia 30303

^{*}Supported in part under National Aeronautics and Space Administration
Grant No. NGR 28-004-021.

[†]Supported in part under National Science Foundation Grant No. GP-38905

Angular Distribution of Photoelectrons from Atomic
Oxygen, Nitrogen, and Carbon

Steven T. Manson*
Department of Physics, Georgia State University
Atlanta, Georgia, 30303, USA

David J. Kennedy
School of Physics, Georgia Institute of Technology
Atlanta, Georgia, 30332, USA
and
§School of Physical Sciences, New University of Ulster
Coleraine, Northern Ireland

Anthony F. Starace†
Behlen Laboratory of Physics, University of Nebraska
Lincoln, Nebraska, 68508, USA

Dan Dill
Department of Chemistry, Boston University
Boston, Massachusetts, 02215, USA

Abstract

The angular distributions of photoelectrons from atomic oxygen, nitrogen, and carbon are calculated. Both Hartree-Fock and Hartree-Slater (Herman-Skillman) wave functions are used for oxygen and the agreement is excellent; thus only Hartree-Slater functions are used for carbon and nitrogen. The pitch angle distribution of photoelectrons is discussed and it is shown that previous approximations of energy independent isotropic or $\sin^2 \theta$ distributions are at odds with our results, which vary with energy. This variation with energy is discussed as is the reliability of these calculations.

*Supported in part by NSF Grant GP-38905.

§Present address.

†Supported in part by NASA Contract NGR 28-004-021.

PHOTOELECTRON ANGULAR DISTRIBUTIONS FOR OPEN-SHELL
ATOMS: A PROBE OF ANISOTROPIC ELECTRON-ION INTERACTIONS

Dan Dill

Dept. of Chemistry, Boston Univ., Boston, Massachusetts 02215 U.S.A.

and

Anthony F. Starace

Behlen Lab. of Physics, Univ. of Nebraska, Lincoln, Nebraska 68508 U.S.A.

and

Steven T. Manson

Dept. of Physics, Georgia State Univ., Atlanta, Georgia 30303 U.S.A.

The photoelectron asymmetry parameter β in LS-coupling is obtained, starting from the representation of β as an expansion into contributions from alternative angular momentum transfers j_t ,¹⁻³ each of which has a characteristic angular distribution. For open-shell atoms the photoelectron-ion interaction is generally anisotropic: photoelectron phase shifts and electric dipole matrix elements depend on both the multiplet term of the residual ion and the total orbital momentum of the outgoing photoelectron channel. Consequently β depends on the term levels of the residual ion and contains contributions from all allowed values of j_t . These findings contradict the independent particle model theory for β ,⁴ which ignores final-state electron-ion interaction and to which our expressions reduce only in the limiting cases of 1) spherically symmetric atoms [e.g., closed-shell atoms] and 2) open-shell atoms for which the electron-ion interaction is isotropic [e.g., very light elements]. Numerical calculations of the asymmetry parameter are presented for atomic oxygen and atomic sulfur to illustrate the theory and to demonstrate the information on electron-ion dynamics that can be obtained from the theoretical and experimental study of β for open-shell atoms.

A general photoionization process in LS-coupling may be represented as:

$$A((l_0^* L_0 S_0) J_0 \pi_0) + \gamma(j, = 1, \pi, = -1) - A'((l_0^{*-1} L_c S_c) J_c \pi_c) + c'(l s j, \pi_c = (-1)^j). \quad (1)$$

Provided the atom is unpolarized and no measurements are made of the orientation of the ion or of the photoelectron's spin, the differential cross section and the asymmetry parameter may be represented as incoherent sums over allowed angular momentum transfers j_t :

Presented at the International Symposium on Electron
and Photon Interactions with Atoms, Stirling, Scotland,
16-19 July 1974. (Plenum Press, to be published).

EFFECTS OF ANISOTROPIC ELECTRON-ION INTERACTION
ON THE PHOTOELECTRON ANGULAR DISTRIBUTION OF OPEN-SHELL ATOMS

Dan Dill

Department of Chemistry, Boston University

Boston, Massachusetts 02215, U.S.A.

Anthony F. Starace

Behlen Laboratory of Physics, The University of Nebraska

Lincoln, Nebraska 68508, U.S.A.

Steven T. Manson

Department of Physics, Georgia State University

Atlanta, Georgia 30303, U.S.A.

ABSTRACT

-- The photoelectron asymmetry parameter β in LS-coupling is obtained, starting from the representation of β as an expansion into contributions from alternative angular momentum transfers j_t , each of which has a characteristic angular distribution. For open-shell atoms the photoelectron-ion interaction is generally anisotropic: photoelectron phase shifts and electric dipole matrix elements depend on both the multiplet term of the residual ion and the total orbital momentum of the outgoing photoelectron channel. Consequently β depends on the term levels of the residual ion and contains contributions from all allowed values of j_t . These findings contradict the independent particle model theory for β , to which our expressions reduce only in the limiting cases of 1) spherically symmetric atoms (e.g., closed-shell atoms) and 2) open-shell atoms for which the electron-ion interaction is isotropic (e.g., very light elements). Numerical results for atomic oxygen and atomic sulfur are shown.

AMERICAN ASTRONOMICAL SOCIETY

Abstract submitted for the One Hundred Forty-Second meeting

Category Other topics, Date Submitted 28 Jan., 1974

Read by J. L. Gardner

On the Photoionization of Carbon Dioxide.

J. L. GARDNER and J. A. R. SAMSON, U. Nebr. - The kinetic energies of photoelectrons ejected from carbon dioxide have been measured for monochromatic radiation of wavelengths varying between 700 to 300 Å. Knowledge of such photoelectron spectra allows a complete picture to be presented of how radiation interacts with this molecule. Data will be presented giving absolute measurements of the partial cross sections for producing carbon dioxide ions in specific states of ionization.

This work was supported by NASA under Grant No. NGR 28-004-021.

Special Instructions:

Paper to be read in session on
Fundamental Spectroscopic Data and
to follow paper by Haddad and
Samson.

James A. R. Samson
Signature of Author
Physics Dept.
Address
University of Nebraska.

We agree to pay \$20 in partial support of the
publication of this abstract in the B.A.A.S.

James A. R. Samson
Signature of authorized agent
Physics Dept.
Address
Univ. of Nebr.
Lincoln, 68508

P. O. Number if required 37973

Signature of Introducing Member
if author is a non-member.

AMERICAN ASTRONOMICAL SOCIETY

Abstract submitted for the One Hundred Forty-Second meeting

Category Other topics, Date Submitted 28 Jan., 1974

Read by G. N. HADDAD

Ionization of Molecules of Astrophysical Interest. G. N. HADDAD and J. A. R. SAMSON, U. Nebr. -
The total absorption cross sections of H_2 , D_2 , O_2 , N_2 , CO , CO_2 , NH_3 , CH_4 , and the rare gases, have been measured at wavelengths down to 100 \AA with a precision of $\pm 3\%$. The efficiency of the absorbed radiation to produce ionization has been measured for several of the above gases and in some cases multiple ionization has been observed. This work was supported by NASA under Grant No. NGR 28-004-021.

Special Instructions:

Paper to be read in session on
Fundamental Spectroscopic Data and
to precede paper by Gardner and
Samson.

James A. R. Samson
Signature of Author
Physics Dept.
Address
University of Nebraska

We agree to pay \$20 in partial support of the
publication of this abstract in the B.A.A.S.

James A. R. Samson
Signature of authorized agent
Physics Dept.
Address
Univ. of Nebr.
Lincoln 68508

P. O. Number if required _____

Signature of Introducing Member
if author is a non-member.

INTERNATIONAL SYMPOSIUM ON
ELECTRON AND PHOTON INTERACTIONS WITH ATOMS
University of Stirling 16-19 July, 1974

MULTIPLE PHOTOIONIZATION OF THE RARE GASES

by

James A.R. Samson and G.N. Haddad

Physics Department, University of Nebraska, Lincoln, Nebr.

The recent advances made in measuring the absolute intensity of radiation in the vacuum ultraviolet spectral region¹ has permitted direct experiments that determine the photoionization yields of gases from their first ionization threshold down to about 100 \AA (i.e., 124 eV). For the rare gases, excluding He, this spectral range covers the thresholds for single, double, and triple photoionization.

The photoionization yield in this context is defined as the average number of charges produced per photon absorbed by the gas. Thus, the yield is simply the average charged state of an ion per photon absorbed. The results distinguish between singly and doubly charged ions but not between doubly and triply charged species.

4th Int. Conf. on Photoionization
Hawaii, 1968

PHOTOIONIZATION CROSS SECTIONS OF THE OUTER s-SUBSHELL
ELECTRONS IN THE RARE GASES

JAMES A. R. SALLON and J. L. DICKLER

Behlen Laboratory of Physics, University of Nebraska

Lincoln, Nebraska 68508

The absolute photoionization cross sections for the outer ns subshells of neon, argon, krypton, and xenon have been measured from their respective ionization thresholds to about 40 eV. The technique of photoelectron spectroscopy was used to determine the ratio of the s to p photoelectrons. Measurements of the total cross sections¹ and the magnitudes of multiple ionization processes² allowed an accurate determination of the subshell cross sections to be made.

The results for Ar, Kr, and Xe clearly show the interference effect between the $ns^2 np^6 \rightarrow ns^2 np^5$ ed transition and the ns transitions as predicted by Amusia et al.,³ who used the random phase approximation with exchange in their calculations. The experimental results for Ar, Kr, and Xe are shown in Figs. 1 - 3. The dashed curves represent the theoretical results of Amusia et al. The actual magnitude of the theoretical results are sensitive to the value of the ns ionization threshold used in the calculations. The theoretical curves for Ar and Kr, shown in Figs. 1 and 2, used the experimental threshold values. The results are in good agreement with experiment. For Xenon the theoretical threshold differs by about 2 eV from the experimental threshold. Although the shape of the two curves agree the magnitudes do not.

2nd Int. Conf. on VUV Rad. 1968
Hawaii

IONIZATION PROCESSES IN MOLECULES

J.A.R. Samson, C.N. Haddad, and J.B. Gardner

Physics Department, University of Nebraska-Lincoln
Lincoln, Nebraska 68505

More than 99% of the integrated photo-ionization absorption of a molecule takes place in the vacuum ultraviolet region of the spectrum. The first threshold for ionization usually occurs between 9 and 16 eV. The maximum ionization cross sections usually lie between 15 and 20 eV. In the present work the total photo-ionization cross sections of most diatomic molecules have been measured from their ionization threshold down to 100 Å. In addition, the probability of producing ions in various degrees of excitation have been measured at many wavelengths. This includes a study of multiple ionization processes.

It has been customary to analyze the structure of total photo-ionization cross section curves in terms of possible ionization thresholds to high lying excited states of the molecule and to possible double ionization states. To provide definitive results in determining the cause of the structure, we have employed techniques to measure the individual or partial ionization processes. The technique of photoelectron spectroscopy has been used to give accurate branching ratios for producing ions in excited states, while recent advances in measuring the absolute photon flux of radiation down to 100 Å have enabled quantitative measurements on the ionization efficiencies to be made.¹ For the gases O₂, N₂, CO, and CO₂ no double ionization processes could be observed. This gives an upper limit of less than 1% for the probability of double ionization.

Invited Paper

Angular Distributions of Photoelectrons
Ejected from Gases*

James A.R. Samson, University of Nebraska

Observations of the angular distributions of photoelectrons ejected from gases were first studied by Bubb in 1924.¹ From these results and subsequent measurements it was established that there was a preponderance of electrons ejected in the direction of the electric field vector. By 1927 Auger and Perrin² had derived an expression for the angular distribution that took the form $(a = b \cos^2 \theta)$, where θ was the angle between the electric field vector and the electron velocity vector. Most of the experiments verified this $\cos^2 \theta$ distribution. Some forty years later interest in this field has been revived. While the early experiments broadly verified the predictions of the new wave mechanics detailed information was lacking. Recent experimental work has shownⁿ that there is a wide variety of electron distributions possible, varying from completely isotropic to $\cos^2 \theta$ type distributions. Results depend on the orbit from which the electron is ejected, on the kinetic energy of the photoelectrons, and on the presence of autoionizing structure. The experimental techniques and results will be reviewed.

* Supported in part by the National Science Foundation and the National Aeronautics and Space Administration.

¹ F.W. Bubb Phys. Rev. 23, 137 (1924).

² P. Auger and F. Perrin, J. Phys. Radium 8, 93 (1927).

Abstract Submitted
for the 1974 Annual Meeting of the
Division of Electron and Atomic Physics
2-4 December 1974

Physical Review
Analytic Subject Index
Number 13.6

Bulletin Subject Heading
Photoionization

Angular Distribution of Photoelectrons from Halogen Atoms.* S. T. MANSON, Georgia S.U., A. F. STARACE, U. of Nebraska, D. DILL, Boston U.--Calculations of the cross section and asymmetry parameter for photoionization of the outer p-subshell of F, Cl, and Br have been carried out. Numerical Hartree-Fock discrete and continuum wavefunctions were employed.¹ The halogens were chosen for study because they are the likeliest group of open-shell atoms to be experimentally investigated.² The electron-ion interaction is found to be anisotropic for Cl and Br as exhibited by the differing phase shifts of the continuum wavefunctions in the various final-state channels. Consequently we find, as in sulfur,³ that the asymmetry parameters for Cl and Br 1) depend on the final state ionic term level and 2) have contributions from all allowed angular momentum transfers.

*Supported by NSF Grant No. GP-38905 and NASA Grant No. NGR 28-004-021.

¹D. J. Kennedy and S. T. Manson, Phys. Rev. A 5, 227 (1972).

²J. Berkowitz, private communication.

³D. Dill, S. T. Manson, and A. F. Starace, Phys. Rev. Letters 32, 971 (1974).

Submitted by

Steven T. Manson

Steven T. Manson
Department of Physics
Georgia State University
33 Gilmer Street, S.E.
Atlanta, Georgia 30303

Abstract Submitted
for the 1974 Annual Meeting of the
Division of Electron and Atomic Physics
2-4 December 1974

Physical Review
Analytic Subject Index
Number 13.6

Bulletin Subject Heading
Photoionization

Behaviour of Partial Photoionization Cross Sections Across a Resonance.* A. F. STARACE, U. of Nebraska

--The behaviour of the total cross section in the neighborhood of an autoionizing resonance is well known.¹ Only recently however has the theoretical² and experimental³ investigation been completed of the striking oscillatory behaviour of the photoelectron asymmetry parameter across a resonance. This recent work motivated the present study of the energy dependence of partial cross sections across autoionizing resonances. General Fano-type¹ formulas for this dependence are obtained. Specific application is made to the behaviour of the various $np^6(^1S) + h\nu \rightarrow np^5(^2P_{3/2,1/2}) + e^-$ photoionization channels in the rare gases in the neighborhood of the $nsnp^6(n+1)p(^1P)$ resonances. In particular, calculations of the $^2P_{3/2}/^2P_{1/2}$ branching ratios (which can be measured by photoelectron spectroscopy) across these resonances are in progress.

*Supported by NASA grant No. NGR 28-004-21.

¹U. Fano, Phys. Rev. 124, 1866 (1961).

²D. Dill, Phys. Rev. A 7, 1976 (1973).

³J. A. R. Samson and J. L. Gardner, Phys. Rev. Letters 31, 1327 (1973).

Submitted by

Anthony F. Starace
Behlen Laboratory of Physics
The University of Nebraska
Lincoln, Nebraska 68503

Abstract Submitted
for the DEAP Meeting of the
American Physical Society
2-4 Dec., 1974

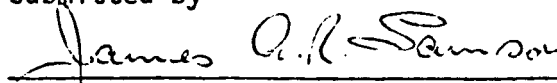
Physical Review
Analytic Subject Index
Number 13.6

Bulletin Subject Heading
in which Paper should be placed

Measurements of Angular Distributions of Photoelectrons with Polarized Radiation.* W.H. HANCOCK and JAMES A.R. SAMSON, Univ. Nebraska--Angular distributions of photoelectrons have been measured by a new technique utilizing polarized vacuum ultraviolet radiation. The photoelectrons were observed in a direction at right angles to the direction of the photon beam, using a cylindrical mirror energy analyzer. The photons were 75% polarized using a three plate reflection polarizer, which could be rotated to change the plane of polarization. Results have been obtained with undispersed 584 Å radiation for the rare gases and selected diatomic molecules. Attempts are currently underway to measure the angular distribution of photoelectrons ejected from atomic oxygen. The method is also being extended to other wavelengths.

*Research supported by the Atmospheric Sciences Section,
National Science Foundation.

Submitted by



James A. R. Samson

Behlen Laboratory of Physics

University of Nebraska

Lincoln, Nebraska 68508

Abstract Submitted
for the DEAP Meeting of the
American Physical Society

2-4 Dec., 1974

Physical Review
Analytic Subject Index
Number

12.5

Bulletin Subject Heading
in which Paper should be placed

Photoion and Photoelectron Spectroscopy
of CO and N₂. J. L. Gardner and JAMES A. R.
SAMSON, Univ. Nebraska--Ion and electron
kinetic energy spectra of CO and N₂ have been
measured at a number of incident wavelengths
extending down to 304 Å. Correlation of the
304 Å spectra shows that the $2\Sigma^+$ state formed
by removal of a 3 σ electron from CO dissociates
to the products C⁺ (2p² 2p⁰) and O (3s' 3d⁰).
Similarly, the corresponding process in N₂
yields products N⁺ (2p³ 3p⁰) and H (2p³ 4s⁰).

Submitted by

James A.R. Samson

Behlen Laboratory of Physics

University of Nebraska

Lincoln, Nebr. 68508